

ADSORPTIVE PROPERTIES OF FLY ASH CARBON

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INTRODUCTION

The driving force behind the development of this research project has been the increasing concerns about the detrimental effects of high carbon carryover into combustion ash. Without the carbon, combustion ash can be utilized in cement industry avoiding environmental implications in landfill operations. Because the carbon surfaces have been structurally altered while passing through the combustor, including the formation of a macro-porous surface, fly ash carbons, after separation from the ash, may constitute a unique precursor for the production of adsorbents. This paper discusses a novel approach for using fly ash carbons in the cleanup of organic pollutants.

Fly Ash Carbon

Fly ash carbon may take a special place amongst the carbon materials that are produced either as a major co-product (e.g. in the pyrolysis of different starting materials for the production of liquids and gases) or processed primarily for the manufacture of active carbons and carbon-carbon composites. The fly ash carbons occur in the residual coal ash as a result of the incomplete combustion process. Due to the increasing applications of activated carbons^{1,2}, this study has been focused on the preparation of cost-effective adsorbents as a substitute for activated carbon materials. Today, only few efforts have been made to investigate the advantages of fly ash carbons as a starting material to produce a powerful adsorbent^{3,4}. The main objective of this study, therefore, has been to explore the possibility of using fly ash carbon as an adsorbent for the removal of organic pollutants including phenols.

Manufacturing and commercialization have not yet been considered for the fly ash carbons, mainly because there still prevails a number of problems related to fly ash carbons. A critical impediment to the utilization of fly ash carbon is the fact that these particles need to be recovered from the ash. Recently the removal of the carbons from fly ash has received major attention, because the mandated lowering of NO_x emissions as a consequence of the Clean Air Act, resulted in an overall increase of unburned coal particles in the ash^{5,6}. This has significant consequences in terms of utilization potential of the ash. Carbon separation allows the recovery of a low LOI (loss on ignition) ash suitable for cement applications^{5,7}, but also entails the concentration of unburned carbon particles that have undergone partial carbonization in the combustion furnace. Once the carbons are recovered the topics that are focused on in this study are (1) what controls the optimum amount of pores in the fly ash carbons, (2) what influences surface morphologies and surface functional groups, and ultimately (3) what controls the potential of fly ash carbons to be activated and upgraded to a commercial product. It should be recognized in this paper that the word carbon is used interchangeably with unburned coal particles.

MATERIALS AND PROCEDURES

Combustion Char Characteristics

The concentration of unburned carbon particles in fly ash varies greatly among ashes produced by different utilities, and the nature of the microscopic carbon forms can also be distinct⁷⁻¹⁰. The fly ash carbons are composed of three petrographically distinguishable types, namely, inertinite, isotropic coke and anisotropic coke; the absolute quantities of which may vary depending on feed stock and boiler conditions⁹. Both coke forms are most likely derived from vitrinite macerals and are artifacts of incomplete combustion. Inertinite is relatively unreactive in the thermal processing of coal and occurs essentially unaltered in the fly ash, while "coke" is produced from melting, devolatilization, swelling, and resolidification of the reactive macerals vitrinite and liptinite. Samples were derived from Midwestern power stations after NO_x conversion. The proportions of isotropic : anisotropic coke: inertinite in 21 fly ashes are shown in Figure 1, indicating that petrographically fly ash carbon fits into three broad ranges.

The residence time of the fly ash carbons in the furnace causes the particle surfaces and in some types of coal particles the entire grains to be perforated with submicron-sized pores. Extensive parallel orientation of individual crystallites in the carbonaceous matrix relates to the porosity of the fly ash carbons, leaving few micro-voids between the crystallites and low micro-porosity in the

precursor phase. For the purpose of this study it was of paramount importance to select a carbon concentrate with a high isotropic carbon fraction as preliminary tests indicated a preferential adsorption capacity for samples enriched in the isotropic "coke". The adsorptive properties of the fly ash carbon may be

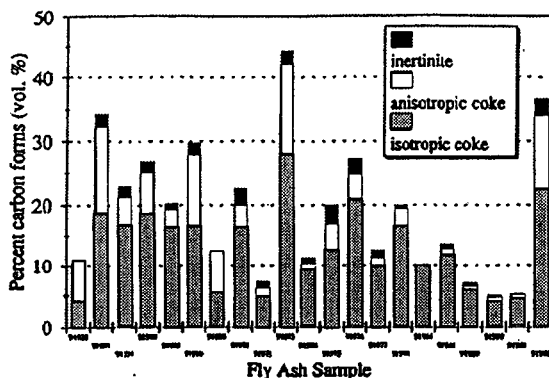
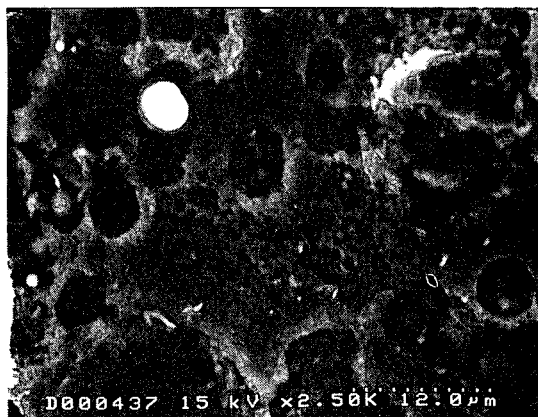


Figure 1 Variations in carbon forms and content of 21 coal combustion fly ash samples. The samples are ASTM C618 Class F (1992 -1994 CAER survey data).

enhanced in physical and/or chemical treatment if the structural order of the individual crystallites and their mutual orientation may be affected by the treatment. Structural differences among the two types of fly ash carbon (isotropic vs. anisotropic coke) were studied using SEM applications and are illustrated in Figures 2 and 3.

Figure 2

SEM image of isotropic carbon grain. Effect of combustion is clearly visible on the surface with process induced macro-porosity. The irregularity of the char surface suggests that partial oxidation must have occurred with increased surface areas and perforated structures at the outside layer of the carbon grains. This porosity may serve as infrastructure for steam and catalysts during activation.



The pore sizes among different isotropic grains vary immensely. During combustion the isotropic char particles were observed to form a macro-porous network of carbonized material. The remaining coke between large pores was subsequently observed at higher magnification. Its surface is irregular and is characterized by the presence of numerous smaller (10^1 nanometer) pores. Intercalated Si-Al-rich fly ash spheres occur in the larger pores within the carbonaceous matrix and aid to stabilize the macro structure of the particles. Figure 3 shows the structural alignment observed in the anisotropic char particles.

Carbon Concentrates

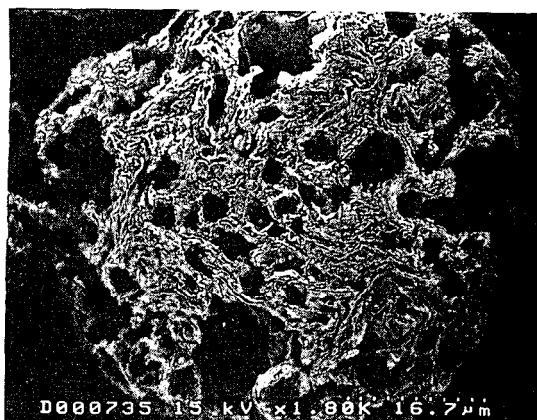
The sample chosen for study for preparing an effective adsorbent from fly ash carbon was focused on a material with a relatively high ratio of isotropic to anisotropic coke. After separation of the fly ash carbon a concentrate sample composed of 81.9 wt % carbon was prepared. Chemical analysis of the carbon concentrate sample is given in Table 1.

TABLE I

Concentrate Sample:	81.9 % C	9.3 % SiO ₂	8.6 % Al ₂ O ₃
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Figure 3

SEM image of anisotropic char particle. The structure clearly indicates structural alignment within the anisotropic particle and less process induced porosity compared to the isotropic coke particle illustrated in Figure 1. The alignment is expected to affect the particle's capacity to be activated.



The manufacture of activated carbons typically involves two main stages, the carbonization of the precursor, and the activation of the resulting char. During carbonization, carbon atoms group themselves into sheets of condensed aromatic ring systems, with an irregular and often bent arrangement. It becomes quite obvious that within the combustion chamber of a coal utility boiler a combination of these processes takes place, affecting each coal particle. Therefore, the experimental part will not involve a separate carbonization step.

EXPERIMENTAL

The carbon concentrate sample (81.9 % C) was used in two types of activation experiments involving (a) physical activation using steam and CO₂ mixture at 900°C, and (b) chemical activation with potassium hydroxide with a 4:1 ratio of carbon : KOH. The synthesis procedure involved dehydration of the concentrate sample at 300°C followed by activation at 900°C for one hour. Activated products were cooled, washed with nitric acid (2mol/ml) and analysed using thermogravimetric analysis (TGA). N₂ adsorption isotherms were analysed for activated and starting materials using an Auatorb-1-MP (QUANTACHROME) instrument to determine changes in surface areas and pore volumes after activation. Surface areas were calculated using the BET equation¹¹.

CHARACTERISTICS OF ACTIVATED FLY ASH CARBON

The macro-porosity of the precursor carbon concentrate was observed to be 19 m²/g. The macropore framework constitutes an infrastructure that may readily allow steam/CO₂ to infiltrate the fly ash carbon during activation, and the intercalation of KOH catalyst, facilitating the development of higher surface areas. The SEM investigations of the activated materials revealed a much rougher surface than that of the precursor, with corresponding increases in BET surface areas. Physical activation for one hour resulted in chars with corresponding BET surface areas ranging from 310 to 380 m²/g for three experiments. Chemical activation for the same amount of time resulted in an enhanced pore development with higher BET surface areas corresponding to 730 to 840 m²/g for four experiments (Table 2). Chemical activation improves not only the total surface area of the fly ash carbon materials, but greatly increases the number of micropores in the processed materials as indicated by differences in micro and meso pore volumes (Table 2).

TABLE 2	Surface Area	Pore Volume [cc/g]
Precursor Fly Ash Carbon	19 m ² /g	-
Physically Activated Precursor	310 - 380 m ² /g 4 samples	Micro=0.18 Meso=0.33
Chemically Activated Precursor	730 - 840 m ² /g 3 samples	Micro=0.41 Meso=0.13

The adsorption capacity of the activated fly ash carbons will depend on the surface area and porosity

of the carbonaceous material as well as the hydrophobicity of the substituent.

Phenol Adsorption Potential

The presence of phenolic compounds and other organic pollutants typically present in water is of paramount concern to health departments. In past efforts the adsorption of these compounds from aqueous solutions, essentially that of phenol and p-nitrophenol, has been studied¹²⁻¹⁴, and major findings indicated that the adsorption of phenols not only depends on the porosity of the adsorbent, but was significantly influenced by surface oxygen complexes present on the activated carbons used. The fact that the fly ash carbons spent a short residence time in an oxidizing furnace at combustion temperatures led to the hypothesis that the process induced surface chemistry of the fly ash carbons may help create a unique precursor material for carbons with affinity to adsorb phenolic compounds.

The experiments included adsorption of phenol (dissolved in aqueous solution) on (a) physically activated fly ash carbon, (b) chemically activated fly ash carbon and (c) commercial carbon (NORIT). Adsorption isotherms were determined for solutions containing 100 mg of dispersed carbon at 298 K. Samples were obtained for different time intervals with a maximum exposure time of 3×10^3 minutes. Phenol adsorption potential was determined spectrophotometrically using maximum UV absorbance wavelength for phenol (269 nm). Results are illustrated in Figure 4.

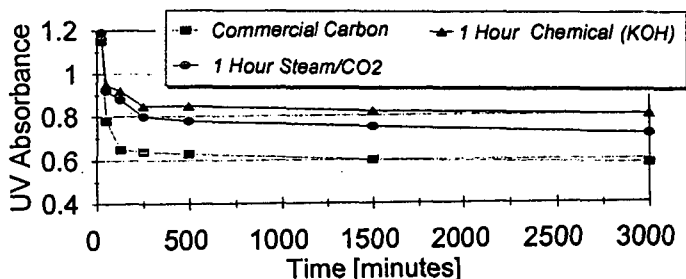


Figure 4 Illustration of the phenol adsorption capacities of (a) physically activated fly ash carbon, (b) chemically activated fly ash carbon and (c) commercial carbon

Results suggest that although chemically activated fly ash carbon has higher surface areas and greater micropore volumes, its adsorption potential for phenol is not much superior over that of the physically activated material. Both physically and chemically activated fly ash carbons exhibit excellent potential for phenol adsorption compared with a commercially available carbon (NORIT).

SUMMARY

Fly ash carbons constitute the char particles that are left in fly ash after the incomplete combustion of coal in the furnace, rendering fly ash above spec for ASTM C618 applications for cement. A beneficiation process allows the selective separation of unburned carbon from fly ash to be used for upgrading into a higher value product. The porosity, surface area, and surface chemistry of fly ash carbons before and after activation were characterized using mercury porosimetry, BET analysis, and liquid-phase adsorption of phenolic compounds

The results of the study underline that adsorbents produced from fly ash carbon as precursor matrix exhibit a remarkable developmental potential. It has been demonstrated in two different ways, by physical activation using a steam/CO₂ treatment and chemical activation using KOH, that activation of the fly ash carbon plays a key role in improving the adsorptive properties. The adsorptive capacity of the fly ash carbon produced either by steam activation and/or chemical treatment with KOH lead to the production of active carbons with an optimal range of micropores and adsorption activity towards phenolic compounds. These observations lead to the conclusion that the maximum capacity and the optimum potential of the fly ash carbons may be improved by applying controlled

experiments that help evaluate the optimum activation temperature, activation time and activation environment. In practical manufacturing and commercialization have not yet been considered for the fly ash carbons, mainly because there still remains a number of problems related to carbonaceous fly ash particles that must be solved in order to achieve high enough performance.

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